PATENT ABSTRACTS OF JAPAN

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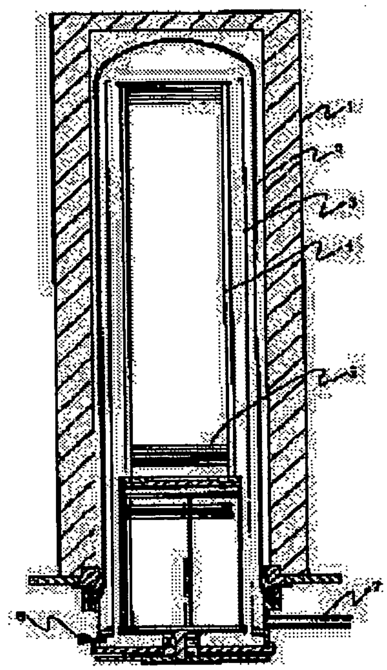
(54) METHOD OF FORMING SILICON DIOXIDE FILM

(57)Abstract:
PROBLEM TO BE SOLVED: To avoid the production of silicon cluster by a method wherein the silicon dioxide film is chemical-vapor-deposited on a substrate meeting a specific pressure reducing requirements in a mixed growing gas with nitrous oxide containing a specific amount of monosilane.
SOLUTION: The lower end of an inner reaction tube 3 is communicated with a gas leading pipe 6 connected to a growing gas supply source so as to supply a growing gas containing SiH4 and N2O to a reaction chamber. Besides, the lower end of an outer reaction tube 2 is communicated with an exhaust pipe 7 so as to exhaust the gas in the reaction chamber. Accordingly, the growing gas led in from the leading pipe 6 runs in the inner reaction tube 3 containing a wafer 5 so as to produce SiO2 at a specific heating temperature for the formation of an SiO2 film on the wafer 5. Through these procedures, the pressure in the reaction chamber is reduced at the state exceeding 40Pa by adjusting the gas supply amount from the gas leading pipe 6 and the exhaust amount from the exhaust pipe 7 so that the ratio of SiH4 of the growing gas may not exceed 2mol% to the total amount of SiH4, and N2O.



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CLAIMS

[Claim(s)]
[Claim 1] The formation approach of the silicon dioxide film characterized by having considered as reduced pressure conditions at least 40Pa or more, and making the rate of the mono silane of said growth gas into 2.0% or less by the mole ratio to the total quantity of a mono silane and nitrous oxide in the approach of making carry out chemical vapor deposition of the silicon dioxide film, and forming it on a substrate in the growth gas containing a mono silane and nitrous oxide.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the approach of forming the silicon dioxide film on a substrate with chemical vapor growth (CVD).
[0002]
[Description of the Prior Art] In the process in which semiconductor devices, such as an MOS mold memory device (MOSRAM) and a static memory component (SRAM), are manufactured, forming gate dielectric film, the passivation film, an interlayer insulation film, etc. with a silicon dioxide (SiO2) on substrates, such as a silicon wafer, is performed. Formation of the silicon dioxide film by chemical vapor deposition (CVD method) loads with the wafer which a fission reactor is made to form, and is performed by supplying growth gas to this fission reactor.
[0003] A mono silane (SiH4) and nitrous oxide (N2O) are contained in growth gas, and, generally the silicon dioxide film (SiO2 film) is generated by SiH4+2N2 O=SiO2+2H2O+4N2 on a wafer under the generation temperature of about 700 degrees C of a fission reactor thru/or about 850 degrees C. In formation of SiO2 film by such conventional CVD method, growth gas used what contains SiH4 2.5% or more by the mole ratio to the total quantity of SiH4 and N2O.
[0004]
[Problem(s) to be Solved by the Invention] However, if it was in formation of SiO2 film by the conventional CVD method, there was a problem that a projection (silicon cluster) with a magnitude of about hundreds of A will be formed in the front face of SiO2 generated film. When SiO2 film with which such a silicon cluster was formed is used as gate dielectric film of for example, a semiconductor memory component, predetermined gate pressure-proofing will not be obtained but the dependability of a component will fall remarkably. For this reason, the wafer with which the silicon cluster has been formed could not be used because of formation of a semiconductor device, but the product yield had fallen remarkably.
[0005] This invention was made in view of the above-mentioned conventional situation, and aims at offering the formation approach of the silicon dioxide film which prevented generating of a silicon cluster.
[0006]
[Means for Solving the Problem] In order to attain the above-mentioned purpose, the formation approach of the silicon dioxide film concerning this invention is characterized by having considered as reduced pressure conditions at least 40Pa or more, and making the rate of the mono silane of said growth gas into 2.0% or less by the mole ratio to the total quantity of a mono silane and nitrous oxide in the approach of making carry out chemical vapor deposition of the silicon dioxide film, and forming it on a substrate, in the growth gas containing a mono silane and nitrous oxide.
[0007] In generation of SiO2 film by the CVD method, a flow and pressure requirement will decline [the growth rate of low voltage past ** and SiO2 film] considerably, and the homogeneity of the thickness distribution of SiO2 film generated on the other hand when the pressure was too high which is not practical will fall. Moreover, when the mole ratio of SiH4 contained in growth gas is not much high, a silicon cluster will occur on SiO2 film generated by

SiH_4 concentration under a reduced pressure condition becoming high beyond the need. so, by the approach of this invention according to claim 1 A practical growth rate is realized by carrying out reduced pressure conditions to more than at least 40Pa (pascal). With this SiH_4 concentration is lowered for the rate of SiH_4 of growth gas as 2% or less by the mole ratio to the total quantity of SiH_4 and N_2O, the absolute magnitude of SiH_4 molecule in growth gas is controlled, and SiO_2 film is formed, preventing generating of a silicon cluster.
[0008] About generating of the silicon cluster in formation of SiO_2 film by the CVD method, if it will be hard coming to generate a silicon cluster if a flow and pressure requirement serves as high pressure, and SiH_4 concentration becomes small, a silicon cluster will stop being able to tending to generate easily. A certain thing [that the relation between this flow and pressure requirement and SiH_4 concentration will form SiO_2 film, without generating a silicon cluster if extent correlation is carried out and these both conditions are combined practically] is possible.

[0009]
[Embodiment of the Invention] The formation approach of the silicon dioxide film concerning this invention is explained based on an example. First, the equipment which enforces the formation approach of the silicon dioxide film concerning this invention is explained with reference to drawing 1 . This equipment is equipped with the boat 4 holding the wafer 5 for membrane formation in the tubed heater 1, the external coil 2 held in the interior of a heater 1, the internal coil 3 held in the interior of the external coil 2, and the internal coil 3. The external coil 2 is forming the reaction chamber which upper limit was closed and connoted the internal coil 3, and upper limit is opened wide and it is opening the internal coil 3 for free passage to the reaction chamber concerned. SiO_2 film is formed in the wafer 5 which this reaction chamber was heated at the heater 1, and was held in the reaction chamber under the predetermined temperature of 700 degrees C thru/or 850 degrees C.
[0010] The gas installation tubing 6 is opened for free passage by the lower limit section of the internal coil 3, and the growth gas which the source of growth gas supply outside drawing is connected to the gas installation tubing 6, and contains SiH_4 and N_2O in a reaction chamber is supplied. Moreover, the exhaust pipe 7 connected to the exhauster outside drawing is opened for free passage by the lower limit section of the external coil 2, and the gas in a reaction chamber is exhausted from an exhaust pipe 7. Therefore, the growth gas introduced from the gas installation tubing 6 flows the inside of the internal coil 3 which held the wafer 5, generates SiO_2 whenever [predetermined stoving temperature] in the bottom, and makes SiO_2 film form on a wafer 5. The pressure in a reaction chamber has come change into a reduced pressure condition 40Pa or more here by adjustment with the gas supply volume from the gas installation tubing 6, and the displacement from an exhaust pipe 7.
[0011] Moreover, at the membrane formation process of SiO_2 film in SiH_4 and N_2O, generally, it is carried out in 700 degrees C - 850 degrees C, a temperature gradient is set up in said temperature requirement towards the upper part from the lower part of a heater 1, and the direction of the lower part of a heater 1 is set as temperature lower than the upper part. Thus, since reactant gas is exhausted and gas concentration becomes low as reactant gas concentration is high and goes up like the lower part of a heater 1, i.e., the reaction chamber bottom, the reason for establishing a temperature gradient is for making thickness in the lower part equivalent from the upper part according to a temperature gradient.
[0012] The pressure in a reaction chamber was made into three kinds, 40Pa, 80Pa, and 160Pa, and SiO_2 film with a thickness of 300A was formed [the rate of SiH_4 contained in growth gas] for the mole ratio and the quantity of gas flow all over the principal plane of the silicon wafer 5 with a diameter of 8 inches as the five following kinds to the total quantity of SiH_4 and N_2O in above equipment. SiH_4 by (1) mole ratio by 1/30 (namely, about 3.4%) and the quantity of gas flow Namely, 35SCCM(s), N_2O by 1050SCCM(s) and (2) mole ratios 1/40 (namely, 2.5%), For SiH_4, 27SCCM(s) and N_2O is 1/50 () at 1050SCCM(s) and (3) mole ratios in a quantity of gas flow. 21SCCM(s) and N_2O by the quantity of gas flow 2.0% Namely, 1050SCCM(s), [SiH_4] (4) — a mole ratio — 1/60 (namely, about 1.7%) and a quantity of gas flow — SiH_4 — by the quantity of gas flow, 15SCCM(s) and N_2O was as 1/70 (namely, about 1.4%) by 1050SCCM(s) and (5) mole

ratios, and SiH4 could be [18SCCM(s) and N2O] five kinds of 1050SCCM(s). The result to which the scale factor 60,000 carried out SEM observation of the SiO2 film formed of this experiment is shown in Table 1 thru/or 3, respectively.
[0013]
[Table 1]
圧力 40Pa

SiH_4 モル比	シリコンクラスタの有無	屈折率	成膜速度 Å／min	膜厚均一性 ±%
1 ／ 30	○	1.29	17.6	3.0 以下
1 ／ 40	○	0.98	14.8	2.8 以下
1 ／ 50	×	0.78	12.4	2.5 以下
1 ／ 60	×	0.66	11.0	2.5 以下
1 ／ 70	×	0.56	10.5	2.5 以下

[0014]
[Table 2]
圧力 80Pa

SiH_4 モル比	シリコンクラスタの有無	屈折率	成膜速度 Å／min	膜厚均一性 ±%
1 ／ 30	○	2.58	31.0	5.0 以下
1 ／ 40	×	1.95	23.8	3.0 以下
1 ／ 50	×	1.57	20.2	3.0 以下
1 ／ 60	×	1.31	18.0	2.8 以下
1 ／ 70	×	1.13	16.1	2.6 以下

[0015]
[Table 3]
圧力 160Pa

SiH_4 モル比	シリコンクラスタの有無	屈折率	成膜速度 Å／min	膜厚均一性 ±%
1 ／ 30	×	5.16	55.2	7.5 以下
1 ／ 40	×	3.90	45.0	7.0 以下
1 ／ 50	×	3.14	36.8	6.0 以下
1 ／ 60	×	2.62	31.4	5.5 以下
1 ／ 70	×	2.26	27.4	4.0 以下

[0016] The observation result about SiO2 film which was formed in the pressure of 40Pa and Table 2 by the pressure of 80Pa, and was formed in Table 3 by 160Pa is shown in Table 1, and it is made to correspond to the mole ratio of SiH4 contained in growth gas in each table, and X mark is described, when existence of a silicon cluster is observed and O mark and existence of a silicon cluster are not observed. In addition, thickness homogeneity measures the thickness of two or more points in the circumferencial direction in a wafer, and the direction of circles of longitude at equal intervals, and takes out deflection to them. Moreover, a membrane formation rate is broken by deposition time amount to the average thickness of a lower wafer into a top in a wafer processing field. Moreover, according to the refractive index, the crystallized state (membraneous quality) of membrane formation can be judged.
[0017] If a flow and pressure requirement serves as high pressure from the above-mentioned table about generating of the silicon cluster in SiO2 formed film, it will be hard coming to

generate a silicon cluster, and if the mole ratio of SiH4 becomes small, it turns out that a silicon cluster stops being able to tending to generate easily. Thus, by generation of SiO2 film by the CVD method, if a pressure is high, the passing speed of SiH4 molecule in growth gas and an N2O molecule can loosen, decomposition of N2O is performed smoothly, and the reason which a silicon cluster will stop being able to generate easily if a flow and pressure requirement serves as high pressure is considered that generating of a silicon cluster is controlled by this. Moreover, the reason which a silicon cluster will stop being able to generate easily if the mole ratio of SiH4 becomes small is considered for the probability for Si atom to serve as the aggregate to fall, when SiH4 concentration in growth gas falls and the absolute magnitude of SiH4 molecule decreases.

[0018] And generating of the silicon cluster in 1/50 or less [then] and SiO2 film does not have reduced pressure conditions in the mole ratio of SiH4 at 40Pa so that clearly from the above-mentioned table. Generating of the silicon cluster in 1/40 or less [then] and SiO2 film did not have reduced pressure conditions in the mole ratio of SiH4 at 80Pa, and generating of the silicon cluster in SiO2 film did not have reduced pressure conditions considering the mole ratio of SiH4 as 1/30 at 160Pa. Therefore, it is possible by setting reduced pressure conditions to 40Pa thru/or 160Pa, and combining these both conditions for the rate of SiH4 of growth gas as below 1/50 (namely, 2.0%) by the mole ratio to the total quantity of SiH4 and N2O to form SiO2 film, without generating a silicon cluster practically.

[0019] If it says from a practical use side, while a membrane formation rate becomes slow, membrane formation time amount will require for 40Pa or less seriously and the amount of the expensive reactant gas used will increase, a serious fault causes the fall of a throughput, as a result delay of a back process by the throughput fall of equipment, and is not suitable for the production process of a semiconductor device. Therefore, it is good to be 2.0 or less-mole ratio conditions, and to choose a pressure and a mole ratio suitably by 40Pa or more, in consideration of practical membrane formation rate thickness homogeneity and not producing a big change of a refractive index, as further shown in drawing 2 .

[0020]

[Effect of the Invention] As explained above, according to the formation approach of the silicon dioxide concerning this invention, by setting up reduced pressure conditions and the mono-silane concentration in growth gas, generating of a silicon cluster can be prevented and the silicon dioxide film can be formed. And reduced pressure conditions are set to at least 40Pa or more, the rate of the mono silane in growth gas is written as 2.0% or less by the mole ratio to the total quantity of a mono silane and nitrous oxide, and the silicon dioxide film with the very high homogeneity of film pressure distribution can be formed with a practical growth rate, without generating a silicon cluster. Therefore, since generating of the silicon cluster in the formed silicon dioxide film can be prevented according to the formation approach of the silicon dioxide concerning this invention as a result, the effectiveness that the semiconductor device excellent in engine performance, such as withstand voltage, can be manufactured also does so.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention] This invention relates to the approach of forming the silicon dioxide film on a substrate with chemical vapor growth (CVD).

[Translation done.]

PRIOR ART

[Description of the Prior Art] In the process in which semiconductor devices, such as an MOS mold memory device (MOSRAM) and a static memory component (SRAM), are manufactured, forming gate dielectric film, the passivation film, an interlayer insulation film, etc. with a silicon dioxide (SiO2) on substrates, such as a silicon wafer, is performed. Formation of the silicon dioxide film by chemical vapor deposition (CVD method) loads with the wafer which a fission reactor is made to form, and is performed by supplying growth gas to this fission reactor.
[0003] A mono silane (SiH4) and nitrous oxide (N2O) are contained in growth gas, and, generally the silicon dioxide film (SiO2 film) is generated by SiH4+2N2 O=SiO2+2H2O+4N2 on a wafer under the generation temperature of about 700 degrees C of a fission reactor thru/or about 850 degrees C. In formation of SiO2 film by such conventional CVD method, growth gas used what contains SiH4 2.5% or more by the mole ratio to the total quantity of SiH4 and N2O.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] As explained above, according to the formation approach of the silicon dioxide concerning this invention, by setting up reduced pressure conditions and the mono-silane concentration in growth gas, generating of a silicon cluster can be prevented and the silicon dioxide film can be formed. And reduced pressure conditions are set to at least 40Pa or more, the rate of the mono silane in growth gas is written as 2.0% or less by the mole ratio to the total quantity of a mono silane and nitrous oxide, and the silicon dioxide film with the very high homogeneity of film pressure distribution can be formed with a practical growth rate, without generating a silicon cluster. Therefore, since generating of the silicon cluster in the formed silicon dioxide film can be prevented according to the formation approach of the silicon dioxide concerning this invention as a result, the effectiveness that the semiconductor device excellent in engine performance, such as withstand voltage, can be manufactured also does so.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, if it was in formation of SiO2 film by the conventional CVD method, there was a problem that a projection (silicon cluster) with a magnitude of about hundreds of A will be formed in the front face of SiO2 generated film. When SiO2 film with which such a silicon cluster was formed is used as gate dielectric film of for example, a semiconductor memory component, predetermined gate pressure-proofing will not be obtained but the dependability of a component will fall remarkably. For this reason, the wafer with which the silicon cluster has been formed could not be used because of formation of a semiconductor device, but the product yield had fallen remarkably.
[0005] This invention was made in view of the above-mentioned conventional situation, and aims at offering the formation approach of the silicon dioxide film which prevented generating of a silicon cluster.

[Translation done.]

MEANS

[Means for Solving the Problem] In order to attain the above-mentioned purpose, the formation approach of the silicon dioxide film concerning this invention is characterized by having considered as reduced pressure conditions at least 40Pa or more, and making the rate of the mono silane of said growth gas into 2.0% or less by the mole ratio to the total quantity of a mono silane and nitrous oxide in the approach of making carry out chemical vapor deposition of the silicon dioxide film, and forming it on a substrate, in the growth gas containing a mono silane and nitrous oxide.
[0007] In generation of SiO2 film by the CVD method, a flow and pressure requirement will decline [the growth rate of low voltage past ** and SiO2 film] considerably, and the homogeneity of the thickness distribution of SiO2 film generated on the other hand when the pressure was too high which is not practical will fall. Moreover, when the mole ratio of SiH4 contained in growth gas is not much high, a silicon cluster will occur on SiO2 film generated by SiH4 concentration under a reduced pressure condition becoming high beyond the need. so, by the approach of this invention according to claim 1 A practical growth rate is realized by carrying out reduced pressure conditions to more than at least 40Pa (pascal). With this SiH4 concentration is lowered for the rate of SiH4 of growth gas as 2% or less by the mole ratio to the total quantity of SiH4 and N2O, the absolute magnitude of SiH4 molecule in growth gas is controlled, and SiO2 film is formed, preventing generating of a silicon cluster.
[0008] About generating of the silicon cluster in formation of SiO2 film by the CVD method, if it will be hard coming to generate a silicon cluster if a flow and pressure requirement serves as high pressure, and SiH4 concentration becomes small, a silicon cluster will stop being able to tending to generate easily. A certain thing [that the relation between this flow and pressure requirement and SiH4 concentration will form SiO2 film, without generating a silicon cluster if extent correlation is carried out and these both conditions are combined practically] is possible.

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[0010] The gas installation tubing 6 is opened for free passage by the lower limit section of the internal coil 3, and the growth gas which the source of growth gas supply outside drawing is connected to the gas installation tubing 6, and contains SiH4 and N2O in a reaction chamber is supplied. Moreover, the exhaust pipe 7 connected to the exhauster outside drawing is opened for

free passage by the lower limit section of the external coil 2, and the gas in a reaction chamber is exhausted from an exhaust pipe 7. Therefore, the growth gas introduced from the gas installation tubing 6 flows the inside of the internal coil 3 which held the wafer 5, generates SiO2 whenever [predetermined stoving temperature] in the bottom, and makes SiO2 film form on a wafer 5. The pressure in a reaction chamber has come change into a reduced pressure condition 40Pa or more here by adjustment with the gas supply volume from the gas installation tubing 6, and the displacement from an exhaust pipe 7.
[0011] Moreover, at the membrane formation process of SiO2 film in SiH4 and N2O, generally, it is carried out in 700 degrees C - 850 degrees C, a temperature gradient is set up in said temperature requirement towards the upper part from the lower part of a heater 1, and the direction of the lower part of a heater 1 is set as temperature lower than the upper part. Thus, since reactant gas is exhausted and gas concentration becomes low as reactant gas concentration is high and goes up like the lower part of a heater 1, i.e., the reaction chamber bottom, the reason for establishing a temperature gradient is for making thickness in the lower part equivalent from the upper part according to a temperature gradient.
[0012] The pressure in a reaction chamber was made into three kinds, 40Pa, 80Pa, and 160Pa, and SiO2 film with a thickness of 300A was formed [the rate of SiH4 contained in growth gas] for the mole ratio and the quantity of gas flow all over the principal plane of the silicon wafer 5 with a diameter of 8 inches as the five following kinds to the total quantity of SiH4 and N2O in above equipment. SiH4 by (1) mole ratio by 1/30 (namely, about 3.4%) and the quantity of gas flow Namely, 35SCCM(s), N2O by 1050SCCM(s) and (2) mole ratios 1/40 (namely, 2.5%), For SiH4, 27SCCM(s) and N2O is 1/50 () at 1050SCCM(s) and (3) mole ratios in a quantity of gas flow. 21SCCM(s) and N2O by the quantity of gas flow 2.0% Namely, 1050SCCM(s), [SiH4] (4) — a mole ratio — 1/60 (namely, about 1.7%) and a quantity of gas flow — SiH4 — by the quantity of gas flow, 15SCCM(s) and N2O was as 1/70 (namely, about 1.4%) by 1050SCCM(s) and (5) mole ratios, and SiH4 could be [18SCCM(s) and N2O] five kinds of 1050SCCM(s). The result to which the scale factor 60,000 carried out SEM observation of the SiO2 film formed of this experiment is shown in Table 1 thru/or 3, respectively.
[0013]
[Table 1]
圧力 40Pa

SiH_4 モル比	シリコンクラスタの有無	屈折率	成膜速度 Å/min	膜厚均一性 ±%
1 / 30	○	1.29	17.6	3.0 以下
1 / 40	○	0.98	14.8	2.8 以下
1 / 50	×	0.78	12.4	2.5 以下
1 / 60	×	0.66	11.0	2.5 以下
1 / 70	×	0.56	10.5	2.5 以下

[0014]
[Table 2]
圧力 80Pa

SiH_4 モル比	シリコンクラスタの有無	屈折率	成膜速度 Å/min	膜厚均一性 ±%
1 / 30	○	2.58	31.0	5.0 以下
1 / 40	×	1.95	23.8	3.0 以下
1 / 50	×	1.57	20.2	3.0 以下
1 / 60	×	1.31	18.0	2.8 以下
1 / 70	×	1.13	16.1	2.6 以下

[0015]
[Table 3]

圧力 160Pa

SiH_4 モル比	シリコンクラスタの有無	屈折率	成膜速度 Å/min	膜厚均一性 ±%
1 / 80	×	5.16	65.2	7.5以下
1 / 40	×	3.90	45.0	7.0以下
1 / 50	×	3.14	36.8	6.0以下
1 / 60	×	2.62	31.4	5.5以下
1 / 70	×	2.26	27.4	4.0以下

[0016] The observation result about SiO2 film which was formed in the pressure of 40Pa and Table 2 by the pressure of 80Pa, and was formed in Table 3 by 160Pa is shown in Table 1, and it is made to correspond to the mole ratio of SiH4 contained in growth gas in each table, and X mark is described, when existence of a silicon cluster is observed and O mark and existence of a silicon cluster are not observed. In addition, thickness homogeneity measures the thickness of two or more points in the circumferencial direction in a wafer, and the direction of circles of longitude at equal intervals, and takes out deflection to them. Moreover, a membrane formation rate is broken by deposition time amount to the average thickness of a lower wafer into a top in a wafer processing field. Moreover, according to the refractive index, the crystallized state (membraneous quality) of membrane formation can be judged.
[0017] If a flow and pressure requirement serves as high pressure from the above-mentioned table about generating of the silicon cluster in SiO2 formed film, it will be hard coming to generate a silicon cluster, and if the mole ratio of SiH4 becomes small, it turns out that a silicon cluster stops being able to tending to generate easily. Thus, by generation of SiO2 film by the CVD method, if a pressure is high, the passing speed of SiH4 molecule in growth gas and an N2O molecule can loosen, decomposition of N2O is performed smoothly, and the reason which a silicon cluster will stop being able to generate easily if a flow and pressure requirement serves as high pressure is considered that generating of a silicon cluster is controlled by this. Moreover, the reason which a silicon cluster will stop being able to generate easily if the mole ratio of SiH4 becomes small is considered for the probability for Si atom to serve as the aggregate to fall, when SiH4 concentration in growth gas falls and the absolute magnitude of SiH4 molecule decreases.
[0018] And generating of the silicon cluster in 1/50 or less [then] and SiO2 film does not have reduced pressure conditions in the mole ratio of SiH4 at 40Pa so that clearly from the above-mentioned table. Generating of the silicon cluster in 1/40 or less [then] and SiO2 film did not have reduced pressure conditions in the mole ratio of SiH4 at 80Pa, and generating of the silicon cluster in SiO2 film did not have reduced pressure conditions considering the mole ratio of SiH4 as 1/30 at 160Pa. Therefore, it is possible by setting reduced pressure conditions to 40Pa thru/or 160Pa, and combining these both conditions for the rate of SiH4 of growth gas as below 1/50 (namely, 2.0%) by the mole ratio to the total quantity of SiH4 and N2O to form SiO2 film, without generating a silicon cluster practically.
[0019] If it says from a practical use side, while a membrane formation rate becomes slow, membrane formation time amount will require for 40Pa or less seriously and the amount of the expensive reactant gas used will increase, a serious fault causes the fall of a throughput, as a result delay of a back process by the throughput fall of equipment, and is not suitable for the production process of a semiconductor device. Therefore, it is good to be 2.0 or less-mole ratio conditions, and to choose a pressure and a mole ratio suitably by 40Pa or more, in consideration of practical membrane formation rate thickness homogeneity and not producing a big change of a refractive index, as further shown in drawing 2 .

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the sectional view showing an example of the equipment for enforcing the approach concerning this invention.
[Drawing 2] It is the graph which shows the relation between mono-silane concentration and the membraneous quality of the silicon dioxide film.
[Description of Notations]
1 Heater
2 External Coil
3 Internal Coil
4 Boat
5 Wafer
6 Gas Installation Tubing
7 Exhaust Pipe

[Translation done.]

* NOTICES *

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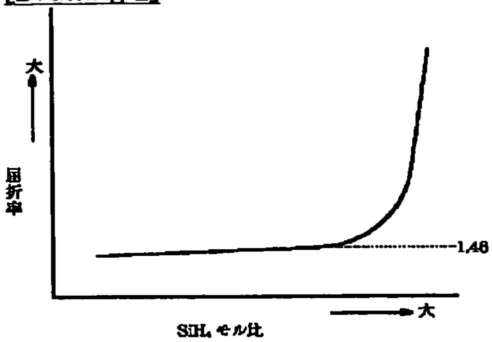
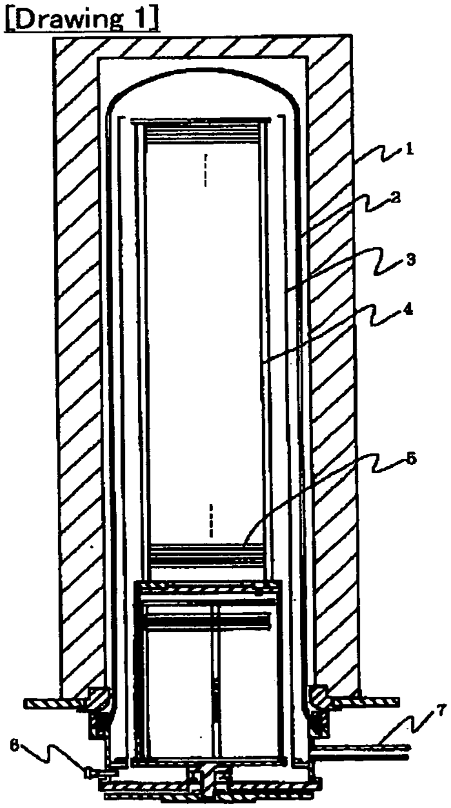
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 2]



[Drawing 1]



[Translation done.]

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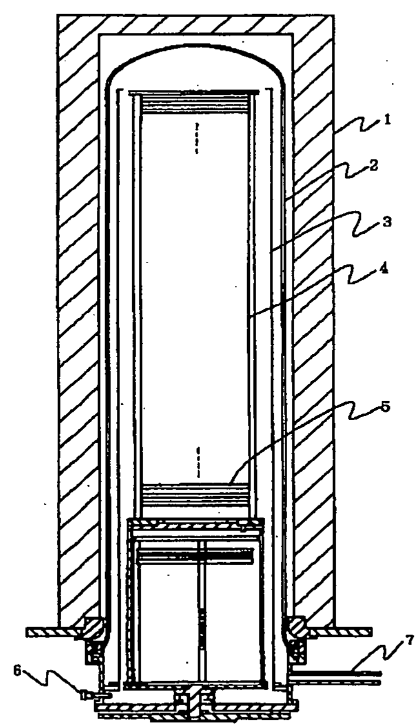
(54)【発明の名称】　二酸化珪素膜の形成方法

(57)【要約】

【課題】　シリコンクラスタの発生を防止して二酸化珪素膜を形成する。

【解決手段】　少なくとも４０Ｐａ以上の減圧条件とし、成長ガスのモノシランの割合をモノシランと亜酸化窒素との合計量に対してモル比で２．０％以下として、基板５上に二酸化珪素膜を化学気相成長させて形成する。これにより、実用的な成長速度を維持しつつ均一な膜圧分布を実現し、かつ、シリコンクラスタの発生を防止して二酸化珪素膜を形成する。



【特許請求の範囲】

【請求項１】 モノシランと亜酸化窒素とを含む成長ガス中で基板上に二酸化珪素膜を化学気相成長させて形成する方法において、少なくとも４０Ｐａ以上の減圧条件とし、前記成長ガスのモノシランの割合をモノシランと亜酸化窒素との合計量に対してモル比で２．０％以下としたことを特徴とする二酸化珪素膜の形成方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は化学的気相成長（ＣＶＤ）により基板上に二酸化珪素膜を形成する方法に関する。

【０００２】

【従来の技術】ＭＯＳ型メモリ素子（ＭＯＳＲＡＭ）やスタティックメモリ素子（ＳＲＡＭ）等の半導体装置を製造する過程において、シリコンウエーハ等の基板上に二酸化珪素（ＳｉO_2）でゲート絶縁膜、パッシベーション膜、層間絶縁膜等を形成することが行われている。化学的気相成長法（ＣＶＤ法）による二酸化珪素膜の形成は、反応炉に成膜させるウエーハを装填し、この反応炉に成長ガスを供給して行われる。

【０００３】成長ガスにはモノシラン（ＳｉH_4）と亜酸化窒素（N_2O）とが含まれており、一般的には反応炉内の約７００℃乃至約８５０℃の生成温度下で、ＳｉH_4＋２N_2O＝ＳｉO_2＋２H_2O＋４N_2により、ウエーハ上に二酸化珪素膜（ＳｉO_2膜）が生成される。このような従来のＣＶＤ法によるＳｉO_2膜の形成においては、成長ガスはＳｉH_4とN_2Oとの合計量に対してＳｉH_4をモル比で２．５％以上含有するものを用いていた。

【０００４】

【発明が解決しようとする課題】しかしながら、従来のＣＶＤ法によるＳｉO_2膜の形成にあっては、生成されたＳｉO_2膜の表面に数百オングストローム程度の大きさの突起（シリコンクラスタ）が形成されてしまうという問題があった。このようなシリコンクラスタが形成されたＳｉO_2膜を、例えば半導体メモリ素子のゲート絶縁膜として用いた場合には、所定のゲート耐圧が得られず、素子の信頼性が著しく低下してしまう。このため、シリコンクラスタが形成されてしまったウエーハは半導体素子の形成のために使用することができず、製品歩留まりが著しく低下してしまっていた。

【０００５】本発明は上記従来の事情に鑑みなされたもので、シリコンクラスタの発生を防止した二酸化珪素膜の形成方法を提供することを目的とする。

【０００６】

【課題を解決するための手段】上記目的を達成するため、本発明に係る二酸化珪素膜の形成方法は、モノシランと亜酸化窒素とを含む成長ガス中で基板上に二酸化珪素膜を化学気相成長させて形成する方法において、少なくとも４０Ｐａ以上の減圧条件とし、前記成長ガスのモノシランの割合をモノシランと亜酸化窒素との合計量に対してモル比で２．０％以下としたことを特徴とする。

【０００７】ＣＶＤ法によるＳｉO_2膜の生成では、圧力条件が低圧すぎるとＳｉO_2膜の成長速度がかなり低下して実用的でない、一方、圧力が高すぎると生成されたＳｉO_2膜の膜厚分布の均一性が低下してしまう。また、成長ガスに含まれるＳｉH_4のモル比があまり高い場合には、減圧状態下でのＳｉH_4濃度が必要以上に高くなって生成されたＳｉO_2膜にシリコンクラスタが発生してしまう。そこで、請求項１に記載の本発明の方法では、減圧条件を少なくとも４０Ｐａ（パスカル）以上として、実用的な成長速度を実現し、これとともに、成長ガスのＳｉH_4の割合をＳｉH_4とN_2Oとの合計量に対してモル比で２％以下として、ＳｉH_4濃度を下げて成長ガス中のＳｉH_4分子の絶対量を抑制し、シリコンクラスタの発生を防止しつつＳｉO_2膜を形成する。

【０００８】ＣＶＤ法によるＳｉO_2膜の形成におけるシリコンクラスタの発生に関して、圧力条件は高圧となればシリコンクラスタは発生し難くなり、ＳｉH_4濃度が小さくなればシリコンクラスタは発生し難くなる傾向がある。この圧力条件とＳｉH_4濃度との関係は或る程度相関しており、実用上はこれら両者の条件を組み合わせると、シリコンクラスタを発生させることなくＳｉO_2膜を形成することが可能である。

【０００９】

【発明の実施の形態】本発明に係る二酸化珪素膜の形成方法を実施例に基づいて説明する。まず、本発明に係る二酸化珪素膜の形成方法を実施する装置を図１を参照して説明する。この装置は、筒状のヒータ１と、ヒータ１の内部に収容された外部反応管２と、外部反応管２の内部に収容された内部反応管３と、内部反応管３内に成膜対象のウエーハ５を保持するボート４とを備えている。外部反応管２は上端が閉じられて内部反応管３を内包した反応室を画成しており、内部反応管３は上端が開放されて当該反応室に連通している。この反応室はヒータ１によって加熱されるようになっており、反応室に収容されたウエーハ５には７００℃乃至８５０℃の所定温度下でＳｉO_2膜が形成される。

【００１０】内部反応管３の下端部にはガス導入管６が連通されており、ガス導入管６には図外の成長ガス供給源が接続されて反応室内にＳｉH_4とN_2Oとを含有する成長ガスを供給するようになっている。また、外部反応管２の下端部には図外の排気装置に接続された排気管７が連通されており、排気管７から反応室内のガスを排気するようになっている。したがって、ガス導入管６から導入された成長ガスはウエーハ５を収容した内部反応管３内を流れ、所定の加熱温度下でＳｉO_2を生成してウエーハ５上にＳｉO_2膜を成膜させる。ここに、ガス導入管６からのガス供給量と排気管７からの排気量との調

整により、反応室内の圧力は４０Ｐａ以上の減圧状態にできるようになっている。

【００１１】また、ＳｉH4とN2OでのＳｉO2膜の成膜工程では、一般的に、７００℃～８５０℃の範囲で行われ、ヒータ１の下部から上部に向けて前記温度範囲内で温度勾配が設定され、ヒータ１の下部の方が上部よりも低い温度に設定される。このように温度勾配を設ける理由は、ヒータ１の下部、即ち反応室の下側程、反応ガス濃度が高く、上方に行くに従って反応ガスが消耗されてガス濃度が低くなることから、温度勾配によって上部から下部での膜厚を同等にするためである。

【００１２】上記の装置において、反応室内の圧力を４０Ｐａ、８０Ｐａ、１６０Ｐａの３通りとし、成長ガス中に含まれるＳｉH4の割合をＳｉH4とN2Oとの合計量に対してモル比及びガス流量を下記の５通りとして、直径８インチのシリコンウエーハ５の主面全面に厚さ３＊＊００オングストロームのＳｉO2膜を形成した。すなわち、（１）モル比で１／３０（すなわち、約３.４％）、ガス流量でＳｉH4が３５ＳＣＣＭ、N2Oが１０５０ＳＣＣＭ、（２）モル比で１／４０（すなわち、２.５％）、ガス流量でＳｉH4が２７ＳＣＣＭ、N2Oが１０５０ＳＣＣＭ、（３）モル比で１／５０（すなわち、２.０％）、ガス流量でＳｉH4が２１ＳＣＣＭ、N2Oが１０５０ＳＣＣＭ、（４）モル比で１／６０（すなわち、約１.７％）、ガス流量でＳｉH4が１８ＳＣＣＭ、N2Oが１０５０ＳＣＣＭ、（５）モル比で１／７０（すなわち、約１.４％）、ガス流量でＳｉH4が１５ＳＣＣＭ、N2Oが１０５０ＳＣＣＭの５通りとした。この実験によって形成されたＳｉO2膜を倍率６万のＳＥＭ観察した結果を表１乃至表３にそれぞれ示す。

【００１３】

【表１】

圧力　40Pa

SiH_4 モル比	シリコンクラスタの有無	屈折率	成膜速度 Å／min	膜厚均一性 ±％
1 ／ 30	○	1.29	17.6	3.0 以下
1 ／ 40	○	0.98	14.8	2.8 以下
1 ／ 50	×	0.78	12.4	2.5 以下
1 ／ 60	×	0.66	11.0	2.5 以下
1 ／ 70	×	0.56	10.5	2.5 以下

【００１４】 ※ ※【表２】

圧力　80Pa

SiH_4 モル比	シリコンクラスタの有無	屈折率	成膜速度 Å／min	膜厚均一性 ±％
1 ／ 30	○	2.58	31.0	5.0 以下
1 ／ 40	×	1.95	23.8	3.0 以下
1 ／ 50	×	1.57	20.2	3.0 以下
1 ／ 60	×	1.31	18.0	2.8 以下
1 ／ 70	×	1.13	16.1	2.6 以下

【００１５】 ★ ★【表３】

圧力　160Pa

SiH_4 モル比	シリコンクラスタの有無	屈折率	成膜速度 Å／min	膜厚均一性 ±％
1 ／ 30	×	5.16	55.2	7.5 以下
1 ／ 40	×	3.90	45.0	7.0 以下
1 ／ 50	×	3.14	36.8	6.0 以下
1 ／ 60	×	2.62	31.4	5.5 以下
1 ／ 70	×	2.26	27.4	4.0 以下

【００１６】表１には圧力４０Ｐａ、表２には圧力８０Ｐａ、表３には１６０Ｐａで形成されたＳｉO2膜についての観察結果を示してあり、それぞれの表には成長ガス中に含まれるＳｉH4のモル比に対応させて、シリコ

ンクラスタの存在が観察された場合には○印、シリコンクラスタの存在が観察されなかった場合にはX印を記してある。なお、膜厚均一性は、ウエーハ内の円周方向、経線方向に等間隔に複数点の膜厚を測定し、偏差を出したものである。また、成膜速度は、ウエーハ処理領域において、上、中、下部のウエーハの平均膜厚に対してデポジション時間で割ったものである。また、屈折率によれば、成膜の結晶状態（膜質）を判断することができる。

【００１７】上記の表から、形成されたSiO_2膜におけるシリコンクラスタの発生に関して、圧力条件が高圧となればシリコンクラスタは発生し難くなり、SiH_4のモル比が小さくなればシリコンクラスタは発生し難くなる傾向があることが判る。このように圧力条件が高圧となればシリコンクラスタが発生し難くなる理由は、ＣＶＤ法によるSiO_2膜の生成では、圧力が高いと成長ガス中のSiH_4分子とN_2O分子との移動速度が緩められて、N_2Oの分解が円滑に行われ、これによって、シリコンクラスタの発生が抑制されると考えられる。また、SiH_4のモル比が小さくなればシリコンクラスタが発生し難くなる理由は、成長ガス中のSiH_4濃度が低下してSiH_4分子の絶対量が少なくなることにより、Ｓｉ原子が集合体となる確率が下がるためと考えられる。

【００１８】そして、上記の表から明らかなように、減圧条件が４０ＰａではSiH_4のモル比を１／５０以下とすればSiO_2膜でのシリコンクラスタの発生はなく、減圧条件が８０ＰａではSiH_4のモル比を１／４０以下とすればSiO_2膜でのシリコンクラスタの発生はなく、減圧条件が１６０ＰａではSiH_4のモル比を１／３０としてもSiO_2膜でのシリコンクラスタの発生はなかった。したがって、減圧条件を４０Ｐａ乃至１６０Ｐａとし、成長ガスのSiH_4の割合をSiH_4とN_2Oとの合計量に対してモル比で１／５０（すなわち、２．０％）以下として、これら両者の条件を組み合わせることにより、実用上はシリコンクラスタを発生させることなくSiO_2膜を形成することが可能である。　＊

＊【００１９】実用面から言えば、４０Ｐａ以下では成膜速度が遅くなり、成膜時間が多大に要することになり、高価な反応ガスの使用量が増えると共に、重大な欠点は装置の処理能力低下によりスループットの低下、ひいては、後工程の遅延を引き起こし、半導体装置の製造工程に適さない。ゆえに、４０Ｐａ以上で、モル比２．０以下の条件であって実用的な成膜速度膜厚均一性、更には図２に示すように屈折率の大きな変化を生じさせないことを考慮して、適宜、圧力とモル比を選択するとよい。

【００２０】

【発明の効果】以上説明したように、本発明に係る二酸化珪素の形成方法によれば、減圧条件と成長ガス中のモノシラン濃度とを設定することにより、シリコンクラスタの発生を防止して二酸化珪素膜を形成することができる。そして、減圧条件を少なくとも４０Ｐａ以上とし、成長ガス中のモノシランの割合をモノシランと亜酸化窒素との合計量に対してモル比で２．０％以下としたため、膜圧分布の均一性が極めて高い二酸化珪素膜をシリコンクラスタを発生させることなく、実用的な成長速度にて形成することができる。したがって、本発明に係る二酸化珪素の形成方法によれば、形成された二酸化珪素膜でのシリコンクラスタの発生を防止できるため、ひいては、絶縁耐圧等の性能に優れた半導体素子を製造することができるという効果も奏する。

【図面の簡単な説明】

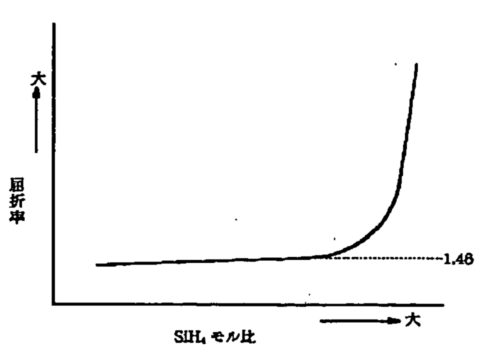
【図１】本発明に係る方法を実施するための装置の一例を示す断面図である。

【図２】モノシラン濃度と二酸化珪素膜の膜質との関係を示すグラフである。

【符号の説明】

1　ヒータ
2　外部反応管
3　内部反応管
4　ボート
5　ウエーハ
6　ガス導入管
7　排気管

【図２】



【図１】